

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

The Isomerisation of 2,5-dihydrothiophene-1, 1-dioxides

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the isomerisation of 2,5-dihydrothiophene-1,1-dioxides to 2,3-dihydrothiophene-1,1-dioxides. The latter compounds are useful intermediates for the manufacture of plasticisers.

According to the present invention there is provided a process for the isomerisation of 2,5-dihydrothiophene-1,1-dioxide and monoalkylated derivatives thereof to 2,3-dihydrothiophene-1,1-dioxide and monoalkyl derivatives thereof in which the 2,5-dihydrothiophene-1,1-dioxide or a monoalkyl derivative thereof is contacted with an alkaline catalyst which is soluble in the reaction mixture and which is a sodium, potassium or lithium hydroxide or alkaline salt, or a strong organic base, in the substantial absence of a substance capable of forming an addition compounds with the 2,5-dihydrothiophene-1,1-dioxide or the monoalkyl derivative thereof or the isomer so formed, and in the presence of a solvent.

Suitable monoalkyl derivatives of 2,5-dihydrothiophene-1,1-dioxide are for example the monomethyl derivatives thereof that is, specifically piperylene sulphone (i.e. the 5-methyl derivative and isoprene sulphone, i.e. the 4-methyl derivative).

In this specification, the phrase "a substance capable of forming an addition compound with the 2,5-dihydrothiophene-1,1-dioxide or the isomer" particularly means, in the case of dihydrothiophene-1,1-dioxide itself, such substances as primary and secondary alcohols and water, which

compounds add to the double bond of the dihydrothiophene-1,1-dioxide ring an -OR radical, where R represents hydrogen, or an alkyl, aryl, alkaryl or aralkyl group. Where a monoalkyl derivative of a dihydrothiophene-1,1-dioxide is used, primary or secondary alcohols may however be present as they will not form addition compounds easily. Water should however be substantially absent.

Suitable solvents for the process of the invention include hydrocarbons, ethers and tertiary alcohols. Tertiary alcohols are preferred however because they normally increase the rate of the isomerisation reaction. It is usually convenient to select a tertiary alcohol which is easily separable, for example by distillation, from the reaction products. Thus tertiary butyl alcohol and tertiary amyl alcohol are particularly suitable for use as solvents in the isomerisation of 2,5-dihydrothiophene-1,1-dioxide, i.e. specifically butadiene sulphone, any unreacted butadiene sulphone being readily removed by heating the reaction products until the sulphone decomposes to butadiene and sulphur dioxide which may then be separated by conventional means.

According to a further feature of the present invention therefore there is provided a process for the production of 2,3-dihydrothiophene-1,1-dioxide in which butadiene sulphone, in the presence of a solvent, is contacted with the alkaline catalyst which is soluble in the reaction mixture in the substantial absence of a substance capable of forming an addition compound with the butadiene sulphone or a product isomer, in which unreacted butadiene sulphone is decomposed to butadiene and sulphur dioxide by heating, the sulphur dioxide and butadiene recovered, re-converted to butadiene sulphone and recycled to the process.

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A molar excess of solvent with regard to the 2,5-dihydrothiophene-1,1-dioxide or its monoalkyl derivative present is preferably used in the process of the invention. Usually 5 molar ratios of solvent to 2,5-dihydrothiophene-1,1-dioxide or its monoalkyl derivative of between about 1:1 and about 3:1 for example about 2:1 are suitable although higher ratios may be used if desired.

10 The alkaline catalysts for use in the process of the invention are the hydroxides and alkaline salts of sodium, potassium and lithium, and strong organic bases, for example tetramethylammonium hydroxide 15 and trimethylbenzylammonium hydroxide according to their solubility characteristics in the reaction mixture. The catalyst is suitably present in small amounts, for example less than 4% by weight based on solvent.

20 Usually less than 1% by weight, based on solvent, of the catalyst is sufficient although in some cases as little as 0.4% by weight based on solvent may be enough. During the reaction a small amount of sulphur dioxide 25 may be liberated because of decomposition of the reaction mixture and this sulphur dioxide may cause a reduction in the activity of the catalyst. It may, therefore be necessary to add further small amounts 30 of the catalyst to the reaction mixture from time to time in order to overcome this.

The process of the invention is preferably carried out at temperature between atmospheric temperature and about 100°C.

35 More preferably, however, it is carried out at temperatures between about 50°C and about 70°C for example at about 65°C, this temperature range giving a reasonably short reaction time without undue decom- 40 position of the reaction mixture to, for example, butadiene and sulphur dioxide in the manner hereinbefore described. The process of the invention is also suitably carried out at substantially atmospheric 45 pressure although pressures above or below atmospheric may be used if desired.

The invention may be carried out in accordance with the following examples, though it is not limited thereto.

50 **EXAMPLE 1**

1 mole of butadiene sulphone is dissolved in 2 moles of tertiary butyl alcohol containing 0.405% by weight, based on the alcohol, of sodium hydroxide. The solution is then stirred at 65°C for 4 hours after which it is neutralised with dilute hydrochloric acid and the tertiary butyl alcohol removed by distillation. The residue is then heated to 180°C and unreacted butadiene sulphone (0.415 moles) decomposes and is removed as butadiene and sulphur dioxide. The product, after crystallisation from ethyl alcohol, is found to be 0.495 moles of 2,3-dihydrothiophene-1,1-dioxide having a melting point of 65 52°C.

EXAMPLE 2

Example 1 is repeated except that 2 moles of tertiary amyl alcohol are used instead of the tertiary butyl alcohol. The product is found to be 0.56 moles of 2,3-dihydrothiophene-1,1-dioxide.

EXAMPLE 3

Example 1 is repeated except that 0.91% by weight, based on the alcohol, of tetra-methylammonium hydroxide is used instead 75 of the sodium hydroxide. 0.475 moles of 2,3-dihydrothiophene-1,1-dioxide is recovered as product following this procedure.

EXAMPLE 4

Example 2 is repeated except that 0.767% 80 by weight, based on the alcohol of tetra-methylammonium hydroxide is used instead of the sodium hydroxide. 0.545 moles of 2,3-dihydrothiophene-1,1-dioxide is recovered using this method.

WHAT WE CLAIM IS:-

1. A process for the isomerisation of 2,5-dihydrothiophene-1,1-dioxide and mono-alkyl derivatives thereof to 2,3-dihydrothiophene-1,1-dioxide and monoalkyl derivatives thereof in which the 2,5-dihydrothiophene-1,1-dioxide or a monoalkyl derivative thereof is contacted with an alkaline catalyst which is soluble in the reaction mixture and which is a sodium, potassium or lithium hydroxide or alkaline salt, or a strong organic base, in the substantial absence of a substance capable of forming an addition compound with the 2,5-dihydrothiophene-1,1-dioxide or the monoalkyl derivative 95 thereof or the isomer so formed, and in the presence of a solvent.

2. A process according to claim 1 in which the monoalkyl derivative of 2,5-dihydrothiophene-1,1-dioxide is a monomethyl derivative thereof.

3. A process according to either of claims 1 and 2 in which the solvent is a tertiary alcohol.

4. A process according to claim 3 in 110 which the tertiary alcohol is easily separable from the reaction products by distillation.

5. A process for the isomerisation of butadiene sulphone according to any preceding claim in which tertiary butyl or tertiary amyl alcohol is used as a solvent, in which any unreacted butadiene sulphone is removed by heating the reaction products until the sulphone decomposes to butadiene 120 and sulphur dioxide which are then separated.

6. A process for the production of 2,3-dihydrothiophene-1,1-dioxide in which butadiene sulphone, in the presence of a 125 solvent, is contacted with an alkaline catalyst which is soluble in the reaction mixture and which is a sodium, potassium or lithium hydroxide or alkaline salt, or a strong organic base, in the substantial 130

- absence of substance capable of forming an addition compound with the butadiene sulphone or the product isomer in which unreacted butadiene sulphone is decomposed to butadiene and sulphur dioxide by heating, the sulphur dioxide and butadiene being recovered, reconverted to butadiene sulphone and recycled to the process.
7. A process according to any preceding claim in which a molar excess of solvent with regard to 2,5-dihydrothiophene-1,1-dioxide or monoalkylated derivative thereof is used.
8. A process according to claim 7 in which the molar ratio of solvent to 2,5-dihydrothiophene-1,1-dioxide or its monoalkyl derivative is between 1:1 and 3:1.
9. A process according to any preceding claim in which the alkaline catalyst is present to the extent of less than 4% by weight of the solvent.
10. A process according to Claim 9 in which less than 1% by weight of the alkaline catalyst based on the solvent is present.
11. A process according to any preceding claim in which further small amounts of the alkaline catalyst are added to the reaction mixture from time to time.
12. A process according to any preceding claim whenever carried out at a temperature between 50°C. and 70°C.
13. A process according to any preceding claim whenever carried out at substantially atmospheric pressure.
14. A process according to Claim 1 whenever carried out substantially as herein described with reference to the Examples.
15. 2,3-Dihydrothiophene - 1,1 - dioxides and monoalkyl derivatives thereof whenever prepared by a process according to any preceding claim.

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